

**Climatological variations of total alkalinity and total inorganic carbon  
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► **To cite this version:**

Elissar Gemayel, Abed El Rahman Hassoun, Mohammed Anis Benallal, Catherine Goyet, P Rivaro, et al.. Climatological variations of total alkalinity and total inorganic carbon Climatological variations of total alkalinity and total inorganic carbon in the Mediterranean Sea surface waters. Earth System Dynamics, European Geosciences Union, 2015, 6, pp.1499-1533. <10.5194/esdd-6-1499-2015>. <hal-01229908>

**HAL Id: hal-01229908**

**<https://hal-univ-perp.archives-ouvertes.fr/hal-01229908>**

Submitted on 17 Nov 2015

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This discussion paper is/has been under review for the journal Earth System Dynamics (ESD). Please refer to the corresponding final paper in ESD if available.

# Climatological variations of total alkalinity and total inorganic carbon in the Mediterranean Sea surface waters

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Received: 28 June 2015 – Accepted: 4 August 2015 – Published: 24 August 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

# ESDD

6, 1499–1533, 2015

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## Abstract

A compilation of several cruises data from 1998 to 2013 was used to derive polynomial fits that estimate total alkalinity ( $A_T$ ) and total inorganic carbon ( $C_T$ ) from measurements of salinity and temperature in the Mediterranean Sea surface waters. The optimal equations were chosen based on the 10-fold cross validation results and revealed that a second and third order polynomials fit the  $A_T$  and  $C_T$  data respectively. The  $A_T$  surface fit showed an improved root mean square error (RMSE) of  $\pm 10.6 \mu\text{mol kg}^{-1}$ . Furthermore we present the first annual mean  $C_T$  parameterization for the Mediterranean Sea surface waters with a RMSE of  $\pm 14.3 \mu\text{mol kg}^{-1}$ . Excluding the marginal seas of the Adriatic and the Aegean, these equations can be used to estimate  $A_T$  and  $C_T$  in case of the lack of measurements. The seven years averages (2005–2012) mapped using the quarter degree climatologies of the World Ocean Atlas 2013 showed that in surface waters  $A_T$  and  $C_T$  have similar patterns with an increasing eastward gradient. The surface variability is influenced by the inflow of cold Atlantic waters through the Strait of Gibraltar and by the oligotrophic and thermohaline gradient that characterize the Mediterranean Sea. The summer-winter seasonality was also mapped and showed different patterns for  $A_T$  and  $C_T$ . During the winter, the  $A_T$  and  $C_T$  concentrations were higher in the western than in the eastern basin, primarily due to the deepening of the mixed layer and upwelling of dense waters. The opposite was observed in the summer where the eastern basin was marked by higher  $A_T$  and  $C_T$  concentrations than in winter. The strong evaporation that takes place in this season along with the ultra-oligotrophy of the eastern basin determines the increase of both  $A_T$  and  $C_T$  concentrations.

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## 1 Introduction

The role of the ocean in mitigating climate change is well known as it absorbs about  $2 \text{ PgCyr}^{-1}$  of anthropogenic  $\text{CO}_2$  (Wanninkhof et al., 2013). Worldwide measurements of surface seawater  $\text{CO}_2$  properties are being conducted as they are important for advancing our understanding of the carbon cycle and the underlying processes controlling it. For instance, the buffer capacity of the  $\text{CO}_2$  system varies with temperature, the distribution of total inorganic carbon and total alkalinity (Omta et al., 2011).

Our understanding of the open-ocean  $\text{CO}_2$  dynamics has drastically improved over the years (Rödenbeck et al., 2013; Sabine et al., 2004; Takahashi et al., 2009; Watson and Orr, 2003). However our understanding of marginal seas such as the Mediterranean remains poor due to the limited measurements combined with the enhanced complexity of the land-ocean interactions. In the Mediterranean Sea, available measurements of the carbonate system are still scarce and only available in specific regions such as the Alboran Sea (Copin-Montégut, 1993), the Gibraltar Strait (Santana-Casiano et al., 2002), the Dyfamed time-series in the Ligurian Sea (Bégovic and Copin-Montégut, 2002; Copin-Montégut and Bégovic, 2002; Touratier and Goyet, 2009) and the Otranto Strait (Krasakopoulou et al., 2011). Large geographical repartition of  $\text{CO}_2$  data are often confined to cruises with a short sampling period (Álvarez et al., 2014; Goyet et al., 2015; Rivaro et al., 2010; Schneider et al., 2007; Touratier et al., 2012). Numerical models have provided some insights of the carbon dynamics in the Mediterranean Sea (Cossarini et al., 2015; D'Ortenzio et al., 2008; Louanchi et al., 2009), but it remains important to constrain the system from in situ measurements to validate their output.

The scarcity of the  $\text{CO}_2$  system measurements in the Mediterranean Sea make it difficult to constrain the  $\text{CO}_2$  uptake in this landlocked area and also limits our understanding of the magnitude and mechanisms driving the natural variability on the ocean carbon system (Touratier and Goyet, 2009). Empirical modeling has been successfully used to study the marine carbon biogeochemical processes such as the estimation of

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biologically produced  $O_2$  in the mixed layer (Keeling et al., 1993), estimation of global inventories of anthropogenic  $CO_2$  (Sabine et al., 2004) and estimation of the  $CaCO_3$  cycle (Koeve et al., 2014). Empirical algorithms were also used to relate limited  $A_T$  and  $C_T$  measurements to more widely available physical parameters such as salinity and temperature (Bakker et al., 1999; Ishii et al., 2004; Lee et al., 2006). The  $A_T$  and  $C_T$  fields can then be used to calculate  $pCO_2$  fields and thus predict the  $CO_2$  fluxes across the air–sea interface (McNeil et al., 2007).

Previous empirical approaches to constrain  $A_T$  in the Mediterranean Sea have only covered selected cruises (Schneider et al., 2007; Touratier and Goyet, 2009) or local areas such as the Dyfamed time-series station or the Strait of Gibraltar (Copin-Montégut, 1993; Santana-Casiano et al., 2002). As for  $C_T$ , empirical models have only been applied to data below the mixed layer depth (MLD) following the equation of Goyet and Davis (1997) at the Dyfamed time series station (Touratier and Goyet, 2009) or using the composite dataset from Meteor 51/2 and Dyfamed (Touratier and Goyet, 2011). Also Lovato and Vichi (2015) proposed an optimal multiple linear model for  $C_T$  using the Meteor 84/3 full water column data. To the best of our knowledge the reconstruction of  $C_T$  in surface waters has not been yet performed in the Mediterranean Sea. This is probably due to the lack of measurements available for previous studies to capture the more complex interplay of biological, physical and solubility processes that drive the  $C_T$  variability in surface waters.

In this study we have compiled  $CO_2$  system measurements from 14 cruises between 1995 and 2013, that allowed us to constrain an improved and new empirical algorithms for  $A_T$  and  $C_T$  in the Mediterranean Sea surface waters. We also evaluated the spatial and seasonal variability of the carbon system in the Mediterranean Sea surface waters, by mapping the 2005–2012 annual and seasonal averages of surface  $A_T$  and  $C_T$  using the quarter degree climatologies of salinity and temperature from the World Ocean Atlas 2013 (WOA13).

## 2 Methods

### 2.1 Surface $A_T$ and $C_T$ data in the Mediterranean Sea

Between 1998 and 2013, there have been multiple research cruises sampling the sea-water properties throughout the Mediterranean Sea. This includes parameters of the carbonate system more specifically  $A_T$ , pH and  $C_T$  and physico-chemical properties of in situ salinity, and temperature. However, the number of the nutrients concentrations was very limited. In this study we have compiled surface water samples between 0 and 10 m depth, totaling 490 and 426 measurements for  $A_T$  and  $C_T$  respectively (Table 1).

### 2.2 Polynomial model for fitting $A_T$ and $C_T$ data

Two polynomial equations for fitting  $A_T$  or  $C_T$  from salinity ( $S$ ) alone or combined with sea surface temperature ( $T$ ) in the surface waters (0–10 m) of the Mediterranean Sea were chosen from the results of the 10-fold cross validation method (Breiman, 1996; Stone, 1974). This type of analysis was previously performed by Lee et al. (2006) for global relationships of  $A_T$  with salinity and temperature. This model validation technique is performed by retaining a single subsample used for testing and training the algorithm on the 9 remaining subsamples. The cross validation process is then repeated 10 times. The best fit is chosen by computing the residuals from each regression model, and computing independently the performance of the selected optimal polynomial on the remaining subsets. The analysis was applied for polynomials of order 1 to 3, and the optimal equation was chosen based on the lowest Root Mean Square Error (RMSE) and the highest coefficient of determination ( $r^2$ ).

To ensure the same spatial and temporal distribution of  $A_T$  and  $C_T$  polynomial fits we only selected stations where  $A_T$  and  $C_T$  were simultaneously measured (Table 1; Fig. 1). To validate the general use of the proposed parameterizations we tested the algorithms with measurements which are not included in the fits (Testing dataset). Hence for the  $A_T$ , 375 and 115 data points are used for the training and testing datasets re-

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spectively. For the  $C_T$  the training dataset is formed from 381 data points and the validation dataset is the same as the testing subset of the 10th fold (45 data points).

## 2.3 Climatological and seasonal mapping of $A_T$ and $C_T$

The climatological and seasonal averages of salinity (Zweng et al., 2013) and temperature (Locarnini et al., 2013) in  $1/4 \times 1/4^\circ$  grid cells were downloaded from the World Ocean Atlas 2013 (WOA13). The seven years averages (2005–2012) and the summer-winter seasonality of  $A_T$  and  $C_T$  fields were mapped at 5 m depth by applying the respective derived algorithms in their appropriate ranges of  $S$  and  $T$ .

## 3 Results and discussion

### 3.1 Fitting $A_T$ in the Mediterranean Sea surface waters

In the surface ocean the  $A_T$  variability is controlled by freshwater addition or the effect of evaporation, and salinity contributes to more than 80 % of the  $A_T$  variability (Millero et al., 1998). In the Mediterranean Sea, several studies have shown that the relationship between  $A_T$  and  $S$  is linear (Copin-Montégut, 1993; Copin-Montégut and Bégovic, 2002; Hassoun et al., 2015b; Rivaro et al., 2010; Schneider et al., 2007). In other studies, the sea surface temperature ( $T$ ) has been included as an additional proxy for changes in surface water  $A_T$  related to convective mixing (Lee et al., 2006; Touratier and Goyet, 2011).

The results of the 10-fold cross validation analysis revealed that the optimal model for  $A_T$  is a second order polynomial in which  $A_T$  is fitted to both  $S$  and  $T$  (Table 2, Eq. 1). A linear relationship between  $A_T$  and  $S$  yields a higher RMSE ( $14.5 \mu\text{mol kg}^{-1}$ ) and a lower  $r^2$  (0.91) than Eq. (1). In a semi-enclosed basin such as the Mediterranean Sea, the insulation and high evaporation as well as the input of rivers and little precipitation leads to a negative freshwater balance (Rohling et al., 2009). The resulting

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et al., 2007), the Transmed cruise in May–June 2007 (Rivaro et al., 2010) or the Meteor 51/2 and the Dyfamed time series station (Touratier and Goyet, 2011).

The proposed algorithm including surface data from multiple cruises, and on a large time span, presents a more global relationship to estimate  $A_T$  from  $S$  and  $T$  than the previously presented equations (Table 3). In Eq. (1),  $T$  and  $S$  contribute to 96 % of the  $A_T$  variability and the RMSE of  $\pm 10.6 \mu\text{mol kg}^{-1}$  presents a significant improvement of the spatial and temporal estimations of  $A_T$  in the Mediterranean Sea surface waters.

### 3.2 Fitting $C_T$ in the Mediterranean Sea surface waters

The surface  $C_T$  concentrations are influenced by lateral and vertical mixing, photosynthesis, oxidation of organic matter and changes in temperature and salinity (Poisson et al., 1993; Takahashi et al., 1993). All these processes are directly or indirectly correlated with sea-surface temperature (Lee et al., 2000). Hence, the parameterization of  $C_T$  in surface waters includes both physical ( $S$  and  $T$ ) and/or biological parameters (Bakker et al., 1999; Bates et al., 2006; Koffi et al., 2010; Lee et al., 2000; Sasse et al., 2013).

The results of the 10-fold cross validation analysis showed that a first order polynome fits  $C_T$  to  $S$  and  $T$  with an RMSE of  $16.25 \mu\text{mol kg}^{-1}$  and  $r^2 = 0.87$ . These values are comparable to the RMSE and  $r^2$  found by previous empirical approaches applied in the Eastern Atlantic (Bakker et al., 1999; Koffi et al., 2010). However we found that a third order polynome improved the RMSE and  $r^2$  of the equation compared to the first order fit (Table 4, Eq. 2). Hence we will retain the large dataset used to develop Eq. (2), where temperature and salinity contribute to 90 % of the  $C_T$  variability encountered in the Mediterranean Sea surface waters. The remaining 10 % could be attributed to the biological and air–sea exchange contributions to the  $C_T$  variability.

The  $C_T$  parameterization developed in this study (Table 4; Eq. 2) showed a higher uncertainty than that of  $A_T$  regarding both RMSE and  $r^2$ . In fact, the interpolation of  $C_T$  in the mixed layer adds a high uncertainty due to the seasonal variability. Also in surface

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waters the  $C_T$  are directly affected by air–sea exchange, and their concentrations will increase in response to the oceanic uptake of anthropogenic  $CO_2$ .

Previous models accounted for the anthropogenic biases in the  $C_T$  measurements by calculating the  $C_T$  rate of increase (Bates, 2007; Lee et al., 2000; Sasse et al., 2013; Takahashi et al., 2014). However in a study, Lee et al. (2000) also did not correct the  $C_T$  concentrations for regions above  $30^\circ$  latitude such as the Mediterranean Sea. In the following we will assess the importance of accounting or not for anthropogenic biases in the  $C_T$  measurements. In that order we downloaded the monthly atmospheric  $pCO_2$  concentrations measured from 1999 to 2013 at the Lampedusa Island Station (Italy) from the World Data Center for Green House Gases (<http://ds.data.jma.go.jp/gmd/wdcgg/>). Following the method described by Sasse et al. (2013), we corrected the  $C_T$  measurements to the nominal year of 2005 and applied the same 10-fold cross validation analysis using data with and without anthropogenic  $C_T$  corrections. We found that the RMSE of the  $C_T$  model trained using measurements with anthropogenic corrections is  $13.9 \mu\text{mol kg}^{-1}$ , which is not significantly different from the model trained using measurements without anthropogenic corrections (Eq. (2);  $\text{RMSE} = 14.3 \mu\text{mol kg}^{-1}$ ).

The yearly increase of  $C_T$  concentrations is difficult to assess due to the wide spatial distribution of the training dataset used to generate Eq. (2). Hence we will refer to the monthly  $C_T$  concentrations measured between 1998 and 2013 at the Dyfamed time-series station. We found that the rate of increase in  $C_T$  concentrations at the Dyfamed site was  $0.99 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (Fig. 3), which is consistent with the anthropogenic  $C_T$  correction rate used in the previous studies of Lee et al. (2000), Bates (2007) and Sasse et al. (2013).

The rate of increase in  $C_T$  concentrations of  $0.99 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  as well as the RMSE difference of  $\pm 0.4 \mu\text{mol kg}^{-1}$  between the two models (with or without anthropogenic corrections) are both smaller than the uncertainty of the  $C_T$  measurements of at least  $\pm 2 \mu\text{mol kg}^{-1}$  (Millero, 2007). A recent study also showed that the uncertainty of the  $C_T$  measurements can be significantly higher than  $\pm 2 \mu\text{mol kg}^{-1}$ , as most laboratories

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reported values of  $C_T$  for the measures that were within a range of  $\pm 10 \mu\text{mol kg}^{-1}$  of the stated value (Bockmon and Dickson, 2015).

Between 1998 and 2013, the  $C_T$  concentrations measured at the Dyfamed time-series station showed a slightly increasing trend ( $r^2 = 0.05$ ). The increase in  $C_T$  concentrations in response to elevated atmospheric  $\text{CO}_2$ , was masked by the high seasonal variations. For example, during the year 1999 the variation in  $C_T$  concentrations reached as high as  $100 \mu\text{mol kg}^{-1}$  (Fig. 4a). Also there is a clear seasonal cycle of surface waters  $C_T$  in the Dyfamed station (Fig. 4b). In the summer, the  $C_T$  starts to increase gradually to reach a maximum of  $2320 \mu\text{mol kg}^{-1}$  during the winter season, after which a gradual decrease is observed to reach a minimum of  $2200 \mu\text{mol kg}^{-1}$  by the end of spring. The seasonal cycle can be explained by the counter effect of temperature and biology on the  $C_T$  variations. During the spring, the increasing effect of warming of  $p\text{CO}_2$  is counteracted by the photosynthetic activity that lowers the  $C_T$ . During the winter, the decreasing effect of cooling on  $p\text{CO}_2$  is counteracted by the upwelling of deep waters rich in  $C_T$  (Hood and Merlivat, 2001; Takahashi et al., 1993). This shows that the  $C_T$  concentrations in surface waters were more affected by the seasonal variations than by anthropogenic forcing.

Considering the small differences in RMSE obtained by the two models, the uncertainties in the  $C_T$  measurements and the clear signal of the seasonal variations; no corrections were made to account for the rising atmospheric  $\text{CO}_2$  concentrations. In regions above  $30^\circ$  latitude such as the Mediterranean Sea, the corrections of  $C_T$  are small considering that the outcropping of deep isopycnal surfaces dilutes the anthropogenic  $\text{CO}_2$  throughout the water column (Lee et al., 2000). Also the dynamic overturning circulation in the Mediterranean Sea plays an effective role in absorbing the anthropogenic  $\text{CO}_2$  and transports it from the surface to the interior of the basins (Hassoun et al., 2015a; Lee et al., 2011).

The residuals of the dataset used to generate the third order polynomial fit for  $C_T$  are presented in Fig. 5a. Most of the  $C_T$  residuals (330 over 381) were within a range of  $\pm 18 \mu\text{mol kg}^{-1}$  ( $1\sigma$ ). In contrast only few residuals (12 over 381) reached up to

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$\pm 50 \mu\text{mol kg}^{-1}$  ( $1\sigma$ ). Applying the  $C_T$  algorithm to the testing dataset (Fig. 5b), yields a mean residual of  $1.48 \pm 19.80 \mu\text{mol kg}^{-1}$  ( $1\sigma$ ) which is close to the uncertainties of our  $C_T$  relationship. The high residuals observed in this study are consistent with the results of the optimal multiple linear regression performed by Lovato and Vichi (2015), where the largest discrepancies between observations and reconstructed data were detected at the surface layer with RMSE higher than  $\pm 20 \mu\text{mol kg}^{-1}$ .

Considering the high uncertainties of the  $C_T$  measurements, the seasonal variations and the anthropogenic forcing; Eq. (2) presents the first parametrization for  $C_T$  in the Mediterranean Sea surface waters, with an RMSE of  $\pm 14.3 \mu\text{mol kg}^{-1}$  ( $1\sigma$ ) and a  $r^2 = 0.90$  (Table 4, Eq. 2).

### 3.3 Spatial and seasonal variability of $A_T$ and $C_T$ in surface waters

The ranges of the 2005–2012 average annual climatologies of the World Ocean Atlas 2013 (WOA13) are from 35.91 to 39.50 for  $S$  and from 16.50 to 23.57 °C for  $T$  (Locarnini et al., 2013; Zweng et al., 2013). However a wider range is observed for the seasonal climatologies, especially during the winter season where  $T$  ranges from 9.05 to 18.43 °C. The estimations of  $A_T$  and  $C_T$  in surface waters from Eqs. (1) and (2) respectively are only applicable in the appropriate ranges of  $T > 13^\circ\text{C}$  and  $36.3 < S < 39.65$ . Hence the surface waters  $A_T$  and  $C_T$  concentrations were mapped only where  $T$  and  $S$  were within the validity range of Eqs. (1) and (2) respectively (Tables 2 and 4). Excluding few near-shore areas and the influence of cold Atlantic Waters in winter, the ranges in which Eqs. (1) and (2) can be applied are within those of the climatological products of  $T$  and  $S$  of the WOA13.

The mapped climatologies for 2005–2012 at 5 m depth showed a strong increase in the eastward gradient for both  $A_T$  and  $C_T$  with the highest concentrations always found in the Eastern Mediterranean (Fig. 6). The minimum values of  $2400 \mu\text{mol kg}^{-1}$  for  $A_T$  and  $2100 \mu\text{mol kg}^{-1}$  for  $C_T$  are found near the Strait of Gibraltar and the maximum

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values of 2650 and 2300  $\mu\text{mol kg}^{-1}$  are found in the Levantine and Aegean sub-basin for  $A_T$  and  $C_T$  respectively.

The  $A_T$  parameterization of this study detects a clear signature of the alkaline waters entering through the Strait of Gibraltar that remains traceable to the Strait of Sicily as also shown by Cossarini et al. (2015). In the eastern basin the positive balance between evaporation and precipitation contributes to the increasing surface  $A_T$ . Local effects from some coastal areas such as the Gulf of Gabes and riverine inputs from the Rhone and Po River are also detected.

Our results for surface  $A_T$  have a similar spatial pattern and range as the annual climatology of Cossarini et al. (2015) which simulates surface  $A_T$  values from 2400 to 2700  $\mu\text{mol kg}^{-1}$ . The main difference is marked in the upper ends of the Adriatic and Aegean sub-basins where our algorithm predicts  $A_T$  values around 2400–2500  $\mu\text{mol kg}^{-1}$ , whereas the analysis of Cossarini et al. (2015) yields a maximum of 2700  $\mu\text{mol kg}^{-1}$  in these regions. Regressions in regions of river input indicate a negative correlation between alkalinity and salinity (Luchetta et al., 2010); hence Eastern marginal seas are expected to have high  $A_T$  due to the freshwater inputs (Cantoni et al., 2012; Souvermezoglou et al., 2010). This shows the sensitivity of our algorithms to temperature and salinity especially in areas that are more influenced by continental inputs such as the Po River and inputs of the Dardanelle in the northern Adriatic and northern Aegean respectively (Fig. 6a).

At the surface, the basin wide distributions of  $C_T$  are affected by physical processes and their gradient is similar to that of  $A_T$  (Fig. 6b). The lowest  $C_T$  concentrations are found in the zone of the inflowing Atlantic water and increases toward the East in part due to evaporation as also shown by Schneider et al. (2010). Our results for surface  $C_T$  have a similar range as the optimal linear regression performed by Lovato and Vichi (2015) which estimates surface  $C_T$  values from 2180 to 2260  $\mu\text{mol kg}^{-1}$ . Moreover, the results show that the Mediterranean Sea is characterized by  $C_T$  values that are much higher (100–200  $\mu\text{mol kg}^{-1}$  higher) than those observed in the Atlantic Ocean at the same latitude (Key et al., 2004).

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As a consequence of uptake of atmospheric  $\text{CO}_2$ , the eastward  $p\text{CO}_2$  increase is parallel to that of  $C_T$  (D'Ortenzio et al., 2008). For example the Ionian and Levantine sub-basin are characterized by a  $p\text{CO}_2$  as high as  $470 \mu\text{atm}$  (Bégovic, 2001), whereas the Algerian sub-basin is characterized by a much lower  $p\text{CO}_2$  of  $310 \mu\text{atm}$  (Calleja et al., 2013). The high  $p\text{CO}_2$  and  $C_T$  encountered in the eastern basin make it a permanent source of atmospheric  $\text{CO}_2$  (D'Ortenzio et al., 2008; Taillandier et al., 2012). Overall the western basin has a lower surface  $C_T$  content than the eastern basin which could be explained by the eastward decrease of the Mediterranean Sea trophic gradient (Lazzari et al., 2012). The higher rate of inorganic carbon consumption by photosynthesis in the western basin can lead to the depletion of  $C_T$  in the surface waters, whereas the ultra-oligotrophic state in the eastern basin can lead to a high remineralization rate that consumes oxygen and enriches surface waters with  $C_T$  (Moutin and Raimbault, 2002).

The magnitude of the seasonal variability between summer and winter for  $A_T$  and  $C_T$  is shown in Fig. 7. Unlike the seven years averages, the seasonal climatological variations (2005–2012) of  $A_T$  have different spatial patterns than those of  $C_T$ . Overall the summer-winter time differences for  $A_T$  have an increasing eastward gradient (Fig. 7a). The largest magnitudes are marked in the Alboran sub-basin with differences reaching up to  $-80 \mu\text{mol kg}^{-1}$ ; the negative difference implies that during the winter inflowing surface Atlantic water has higher  $A_T$  concentrations than in summer. Higher winter than summer time  $A_T$  concentrations are also observed in the Balearic, Ligurian and the South-western Ionian sub-basins but with a less pronounced seasonality ( $\sim -30 \mu\text{mol kg}^{-1}$ ). For these three sub-basins, the  $C_T$  has a higher summer-winter magnitude than  $A_T$  ( $\sim -70 \mu\text{mol kg}^{-1}$ ). The winter cooling of surface waters increases their density and promotes a mixing with deeper water. Thus, the enrichment in winter time likely reflects the upwelling of deep waters that have accumulated  $A_T$  and  $C_T$  from the remineralization of organic matter, respiration and the dissolution of  $\text{CaCO}_3$ . The seasonality is more pronounced for  $C_T$ , which likely reflects the stronger response of  $C_T$  to biological processes than  $A_T$  (Takahashi et al., 1993).

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In the Algerian sub-basin and along the coasts of Tunisia and Libya, the seasonality is inversed with higher  $A_T$  and  $C_T$  concentrations prevailing in the summer. The African coast is an area of coastal downwelling during the winter season. However, during summer the coastal upwelling appears in response to turning of the wind near the coast toward the West (Bakun and Agostini, 2001). In general, the magnitude of the  $A_T$  seasonal variability is higher in summer than in winter for the eastern basin and more particularly in the Ionian and Levantine sub-basins. During this season strong evaporation takes place and induce an increase of  $A_T$  concentrations (Schneider et al., 2007). In the eastern basin, the high evaporation during the summer has a smaller effect on the  $C_T$ , and magnitudes reach their maxima in the Levantine sub-basin ( $\sim +20 \mu\text{mol kg}^{-1}$ ). During winter time the western basin and South East of Sicily appear to be dominated by higher  $C_T$  concentrations than the rest of the eastern basin, where the summer  $C_T$  concentrations are prevailing (Fig. 7b). During winter the high  $C_T$  concentrations that coincide with low SST in the western basin, could result from the deepening of the mixed layer and could be enhanced by the upwelling associated with the Tramontane-Mistral winds that blow from the southern of France and reach the Balearic Islands and the Spanish coast.

## 4 Summary

The  $A_T$  and  $C_T$  algorithms are derived from a compilation of 490 and 426 quality controlled surface measurements respectively, collected between 1999 and 2013 in the Mediterranean Sea. A second order polynomial relating  $A_T$  to both  $S$  and  $T$  yielded a lower RMSE ( $\pm 10.4 \mu\text{mol kg}^{-1}$ ) and a higher  $r^2$  (0.96) than a linear fit deriving  $A_T$  from  $S$  alone. This confirmed the important contribution of temperature to the  $A_T$  variability. Hence, temperature should be included in future algorithms to help better constrain the surface  $A_T$  variations. The proposed second order polynomial had a lower RMSE than other studies when we applied their respective algorithms to the same training dataset.



In this study we propose an improved and global relationship to estimate the  $A_T$  spatial and temporal variations in the Mediterranean Sea surface waters.

The  $C_T$  parameterization is a first attempt to estimate the surface variations in the Mediterranean Sea. A third order polynomial is suggested to fit the  $C_T$  to  $T$  and  $S$  with a RMSE of  $\pm 14.3 \mu\text{mol kg}^{-1}$ . The biological contributions to the  $C_T$  variations were less pronounced than the physical processes. The contributions of to the physical processes and biology to the  $C_T$  variability were 90 and 10% respectively. In terms of anthropogenic forcing, the  $C_T$  rate of increase of  $0.99 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  was significantly lower than the uncertainty of the measurements than can reach  $\pm 10 \mu\text{mol kg}^{-1}$  between different laboratories. Moreover the  $C_T$  concentrations were more affected by the seasonal variations than the increase of atmospheric  $\text{CO}_2$ .

We propose to use Eqs. (1) and (2) for the estimation of surface  $A_T$  and  $C_T$  in the Mediterranean Sea when salinity and temperature of the area are available and are in the appropriate ranges of the equations. However in the Eastern marginal seas especially the northern Adriatic and northern Aegean there is a need to develop a more specific equation that minimizes the errors in these areas. Hence, it is important to enrich the existing dataset by an extensive sampling program such as the Med-SHIP initiative (CIESM, 2012) in order to improve the modeling of the carbonate system over the whole Mediterranean Sea.

*Acknowledgements.* The authors would like to thank all parties that have contributed to the data provision in particular:

- The Sesame IT4 and Moose-GE cruise data were provided through SeaDataNet - Pan-European infrastructure for ocean and marine data management (<http://www.seadatanet.org>).
- The DYFAMED time series have been provided by the Oceanological Observatory of Villefranche-sur-Mer (L. Coppola). This project is funded by CNRS-INSU and ALLENNVI through the MOOSE observing network.
- The Transmed cruise data were provided by Rivaro, P., Russo, A. and Kovacevic, V. The Transmed cruise is part of the VECTOR Project, funded by: the Ministry of Education,

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University and Research, the Ministry of Economy and Finance, the Ministry of the Environment and Protection of Natural Resources and the Ministry of Agriculture and Forestry with an Integrated Special Fund for Research (FISR).

- The MedSEA 2013 cruise data were provided by the University of Perpignan Via Domitia: “Institut de Modélisation et d’Analyse en Géo-Environnements et Santé, ESPACE-DEV” (Goyet, C. and Hassoun, A. E. R.). This project was funded by the EC “Mediterranean Sea Acidification in a changing climate” project (MedSeA; grant agreement 265 103).

Authors are also grateful to the National Council for Scientific Research (CNRS) in Lebanon for the PhD thesis scholarship granted to Miss Gemayel Elissar.

**References**

- Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., Mintrop, L., Luchetta, A., Cantoni, C., Schroeder, K., and Civitarese, G.: The CO<sub>2</sub> system in the Mediterranean Sea: a basin wide perspective, *Ocean Sci.*, 10, 69–92, doi:10.5194/os-10-69-2014, 2014.
- Bakker, D. C. E., de Baar, H. J. W., and de Jong, E.: The dependence on temperature and salinity of dissolved inorganic carbon in East Atlantic surface waters, *Mar. Chem.*, 65, 263–280, 1999.
- Bakun, A. and Agostini, V. N.: Seasonal patterns of wind-induced upwelling/downwelling in the Mediterranean Sea, *Sci. Mar.*, 65, 243–257, 2001.
- Bates, N. R.: Interannual variability of the oceanic CO<sub>2</sub> sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades, *J Geophys. Res.*, 112, C09013, doi:10.1029/2006jc003759, 2007.
- Bates, N. R., Pequignot, A. C., and Sabine, C. L.: Ocean carbon cycling in the Indian Ocean: 1. Spatiotemporal variability of inorganic carbon and air-sea CO<sub>2</sub> gas exchange, *Global Biogeochem. Cy.*, 20, GB3020, doi:10.1029/2005gb002491, 2006.
- Bégovic, M.: Contribution à l’étude du système des carbonates en Méditerranée, Distribution et variation spatio-temporelle de la pression partielle de CO<sub>2</sub> dans les eaux superficielles du bassin Liguro-Provençal, 2001, Thèse, Université Paris, Paris, 303 pp., 2001.
- Bégovic, M. and Copin-Montégut, C.: Processes controlling annual variations in the partial pressure of CO<sub>2</sub> in surface waters of the central northwestern Mediterranean Sea (Dyfed site), *Deep-Sea Res. Pt. II*, 49, 2031–2047, 2002.

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Bégovic, M. and Copin, C.: Alkalinity and pH measurements on water bottle samples during THALASSA cruise PROSOPE, <http://doi.pangaea.de/10.1594/PANGAEA.805265> (last access: 20 August 2015), 2013.

Bockmon, E. E. and Dickson, A. G.: An inter-laboratory comparison assessing the quality of seawater carbon dioxide measurements, *Mar. Chem.*, 171, 36–43, 2015.

Breiman, L.: Stacked regressions, *Mach. Learn.*, 24, 49–64, 1996.

Calleja, M. L., Duarte, C. M., Álvarez, M., Vaquer-Sunyer, R., Agustí, S., and Herndl, G. J.: Prevalence of strong vertical CO<sub>2</sub> and O<sub>2</sub> variability in the top meters of the ocean, *Global Biogeochem. Cy.*, 27, 941–949, 2013.

Cantoni, C., Luchetta, A., Celio, M., Cozzi, S., Raicich, F., and Catalano, G.: Carbonate system variability in the Gulf of Trieste (North Adriatic Sea), *Estuar. Coast. Shelf S.*, 115, 51–62, 2012.

CIESM: Designing Med-SHIP: a Program for repeated oceanographic surveys, CIESM, Monaco, 164 pp., 2012.

Copin-Montégut, C.: Alkalinity and carbon budgets in the Mediterranean Sea, *Global Biogeochem. Cy.*, 7, 915–925, 1993.

Copin-Montégut, C. and Bégovic, M.: Distributions of carbonate properties and oxygen along the water column (0–2000 m) in the central part of the NW Mediterranean Sea (Dyfamed site): influence of winter vertical mixing on air–sea CO<sub>2</sub> and O<sub>2</sub> exchanges, *Deep-Sea Res. Pt. II*, 49, 2049–2066, 2002.

Cossarini, G., Lazzari, P., and Solidoro, C.: Spatiotemporal variability of alkalinity in the Mediterranean Sea, *Biogeosciences*, 12, 1647–1658, doi:10.5194/bg-12-1647-2015, 2015.

D’Ortenzio, F., Antoine, D., and Marullo, S.: Satellite-driven modeling of the upper ocean mixed layer and air–sea CO<sub>2</sub> flux in the Mediterranean Sea, *Deep-Sea Res. Pt. I*, 55, 405–434, 2008.

Goyet, C. and Davis, D.: Estimation of total CO<sub>2</sub> concentration throughout the water column, *Deep-Sea Res. Pt. I*, 44, 859–877, 1997.

Goyet, C., Hassoun, A. E. R., and Gemayel, E.: Carbonate system during the May 2013 Med-Sea cruise, <http://doi.pangaea.de/10.1594/PANGAEA.841933>, last access: 20 August 2015.

Hassoun, A. E. R., Gemayel, E., Krasakopoulou, E., Goyet, C., Abboud-Abi Saab, M., Guglielmi, V., Touratier, F., and Falco, C.: Acidification of the Mediterranean Sea from anthropogenic carbon penetration, *Deep-Sea Res. Pt. I*, 102, 1–15, 2015a.

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Hassoun, A. E. R., Gemayel, E., Krasakopoulou, E., Goyet, C., Abboud-Abi Saab, M., Ziveri, P., Touratier, F., Guglielmi, V., and Falco, C.: Modeling of the total alkalinity and the total inorganic carbon in the Mediterranean Sea, *J. Water Resour. Ocean Sci.*, 4, 24–32, 2015b, <http://www.ocean-sci.net/4/24/2015/>.

Hood, E. M. and Merlivat, L.: Annual to interannual variations of  $f\text{CO}_2$  in the northwestern Mediterranean Sea: results from hourly measurements made by CARIOCA buoys, 1995–1997, *J. Mar. Res.*, 59, 113–131, 2001.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-2, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618899, 2007a.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-3, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618898, 2007b.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-4, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618897, 2007c.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-5, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618896, 2007d.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-6, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618895, 2007e.

Huertas, E.: Hydrochemistry measured on water bottle samples during Garcia del Cid cruise GIFT-1, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618816, 2007f.

Huertas, E.: Hydrochemistry measured on water bottle samples during Garcia del Cid cruise GIFT-2, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618815, 2007g.

Huertas, E.: Hydrochemistry measured on water bottle samples during Garcia del Cid cruise GIFT-3, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618814, 2007h.

Hydes, D., Jiang, Z., Hartman, M. C., Campbell, J. M., Hartman, S. E., Pagnani, M. R., and Kelly-Gerrey, B. A.: Surface DIC and TALK measurements along the M/V Pacific Celebes

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VOS line during the 2007–2012 cruises, available at: [http://cdiac.ornl.gov/ftp/oceans/VOS\\_Pacific\\_Celebes\\_line/](http://cdiac.ornl.gov/ftp/oceans/VOS_Pacific_Celebes_line/), last access: 20 August 2015, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/OTG.VOS\_PC\_2007-2012, 2012.

- 5 Ishii, M., Saito, S., Tokieda, T., Kawano, T., Matsumoto, K., and Inoue, H. Y.: Variability of surface layer CO<sub>2</sub> parameters in the western and Central Equatorial Pacific, in: *Global Environmental Change in the Ocean and on Land*, edited by: Shiyomi, M. K. H., Koizumi, H., Tsuda, A., and Awaya, Y., TERRAPUB, Tokyo, 2004.
- Keeling, R. F., Najjar, R. P., Bender, M. L., and Tans, P. P.: What atmospheric oxygen measurements can tell us about the global carbon cycle, *Global Biogeochem. Cy.*, 7, 37–67, 1993.
- 10 Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T. H.: A global ocean carbon climatology: results from global data analysis project (GLODAP), *Global Biogeochem. Cy.*, 18, GB4031, doi:10.1029/2004gb002247, 2004.
- 15 Koeve, W., Duteil, O., Oschlies, A., Kähler, P., and Segschneider, J.: Methods to evaluate CaCO<sub>3</sub> cycle modules in coupled global biogeochemical ocean models, *Geosci. Model Dev.*, 7, 2393–2408, doi:10.5194/gmd-7-2393-2014, 2014.
- Koffi, U., Lefèvre, N., Kouadio, G., and Boutin, J.: Surface CO<sub>2</sub> parameters and air-sea CO<sub>2</sub> flux distribution in the Eastern Equatorial Atlantic Ocean, *J. Marine Syst.*, 82, 135–144, 2010.
- 20 Krasakopoulou, E., Souvermezoglou, E., and Goyet, C.: Anthropogenic CO<sub>2</sub> fluxes in the Otranto Strait (E. Mediterranean) in February 1995, *Deep-Sea Res. Pt. I*, 58, 1103–1114, 2011.
- Lazzari, P., Solidoro, C., Ibello, V., Salon, S., Teruzzi, A., Béranger, K., Colella, S., and Crise, A.: Seasonal and inter-annual variability of plankton chlorophyll and primary production in the Mediterranean Sea: a modelling approach, *Biogeosciences*, 9, 217–233, doi:10.5194/bg-9-217-2012, 2012.
- 25 Lee, K., Wanninkhof, R., Feely, R. A., Millero, F. J., and Peng, T.-H.: Global relationships of total inorganic carbon with temperature and nitrate in surface seawater, *Global Biogeochem. Cy.*, 14, 979–994, 2000.
- 30 Lee, K., Tong, L. T., Millero, F. J., Sabine, C. L., Dickson, A. G., Goyet, C., Park, G.-H., Wanninkhof, R., Feely, R. A., and Key, R. M.: Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophys. Res. Lett.*, 33, L19605, doi:10.1029/2007gl027207, 2006.

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- Lee, K., Sabine, C. L., Tanhua, T., Kim, T.-W., Feely, R. A., and Kim, H.-C.: Roles of marginal seas in absorbing and storing fossil fuel CO<sub>2</sub>, *Energ. Environ. Sci.*, 4, 1133–1146, 2011.
- Locarnini, R. A., Mishonov, A. V., Antonov, J. I., Boyer, T. P., Garcia, H. E., Baranova, O. K., Zweng, M. M., Paver, C. R., Reagan, J. R., Johnson, D. R., Hamilton, M., and Seidov, D.: World Ocean Atlas 2013, Volume 1: Temperature, NOAA Atlas NESDIS 73, Silver Spring, MD, 33 pp., 2013.
- Louanchi, F., Boudjakdji, M., and Nacef, L.: Decadal changes in surface carbon dioxide and related variables in the Mediterranean Sea as inferred from a coupled data-diagnostic model approach, *ICES J. Mar. Sci.*, 66, 1538–1546, 2009.
- Lovato, T. and Vichi, M.: An objective reconstruction of the Mediterranean sea carbonate system, *Deep-Sea Res. Pt. I*, 98, 21–30, 2015.
- Luchetta, A., Cantoni, C., and Catalano, G.: New observations of CO<sub>2</sub> induced acidification in the northern Adriatic Sea over the last quarter century, *Chem. Ecol.*, 26, 1–17, 2010.
- McNeil, B. I., Metzl, N., Key, R. M., Matear, R. J., and Corbiere, A.: An empirical estimate of the Southern Ocean air-sea CO<sub>2</sub> flux, *Global Biogeochem. Cy.*, 21, GB3011, doi:10.1029/2007gb002991, 2007.
- Medar-Group: MEDATLAS 2002, Mediterranean and Black Sea database of temperature, salinity and biochemical parameters, Climatological Atlas, IFREMER, Plouzane, France, 2002.
- Millero, F. J.: The Marine inorganic carbon cycle, *Chem. Rev.*, 107, 308–341, 2007.
- Millero, F. J., Lee, K., and Roche, M.: Distribution of alkalinity in the surface waters of the major oceans, *Mar. Chem.*, 60, 111–130, 1998.
- Moutin, T. and Raimbault, P.: Primary production, carbon export and nutrients availability in western and Eastern Mediterranean Sea in early summer 1996 (MINOS cruise), *J. Mar. Syst.*, 33, 273–288, 2002.
- Omta, A. W., Dutkiewicz, S., and Follows, M. J.: Dependence of the ocean–atmosphere partitioning of carbon on temperature and alkalinity, *Global Biogeochem. Cy.*, 25, GB1003, doi:10.102/2010gb003839, 2011.
- Perez, F. F., Rios, A. F., Pelegri, J. L., de la Paz, M., Alonso, F., Royo, E., Velo, A., Garcia-Ibanez, M., and Padin, X. A.: Carbon Data Obtained During the R/V Hesperides Cruise in the Atlantic Ocean on CLIVAR Repeat Hydrography Section A17, FICARAM XV, (20 March–2 May 2013), available at: [http://cdiac.ornl.gov/ftp/oceans/CLIVAR/A17\\_FICARAM\\_XV\\_2013/](http://cdiac.ornl.gov/ftp/oceans/CLIVAR/A17_FICARAM_XV_2013/), last access: 20 August 2015, Carbon Dioxide Information Analysis

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Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/OTG.CLIVAR\_FICARAM\_XV, 2013.

Poisson, A., Metzl, N., Brunet, C., Schauer, B., Bres, B., Ruiz-Pino, D., and Louanchi, F.: Variability of sources and sinks of CO<sub>2</sub> in the western Indian and southern oceans during the year 1991, *J. Geophys. Res.*, 98, 22759–22778, 1993.

Rivaro, P., Messa, R., Massolo, S., and Frache, R.: Distributions of carbonate properties along the water column in the Mediterranean Sea: spatial and temporal variations, *Mar. Chem.*, 121, 236–245, 2010.

Rödenbeck, C., Keeling, R. F., Bakker, D. C. E., Metzl, N., Olsen, A., Sabine, C., and Heimann, M.: Global surface-ocean pCO<sub>2</sub> and sea–air CO<sub>2</sub> flux variability from an observation-driven ocean mixed-layer scheme, *Ocean Sci.*, 9, 193–216, doi:10.5194/os-9-193-2013, 2013.

Rohling, E. J., Abu-Zied, R. H., Casford, J. S. L., Hayes, A., and Hoogakker, B. A. A.: The marine environment: present and past, in: *The Physical Geography of the Mediterranean*, edited by: Woodward, J. C., Oxford University Press, 2009.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A. F.: The oceanic sink for anthropogenic CO<sub>2</sub>, *Science*, 305, 367–371, 2004.

Santana-Casiano, J. M., Gonzalez-Davila, M., and Laglera, L. M.: The carbon dioxide system in the Strait of Gibraltar, *Deep-Sea Res. Pt. II*, 49, 4145–4161, 2002.

Sasse, T. P., McNeil, B. I., and Abramowitz, G.: A novel method for diagnosing seasonal to inter-annual surface ocean carbon dynamics from bottle data using neural networks, *Biogeosciences*, 10, 4319–4340, doi:10.5194/bg-10-4319-2013, 2013.

Schneider, A., Wallace, D. W. R., and Körtzinger, A.: Alkalinity of the Mediterranean Sea, *Geophys. Res. Lett.*, 34, L15608, doi:10.1029/2006gl028842, 2007.

Schneider, A., Tanhua, T., Körtzinger, A., and Wallace, D. W. R.: High anthropogenic carbon content in the Eastern Mediterranean, *J. Geophys. Res.*, 115, C12050, doi:10.1029/2010jc006171, 2010.

Schneider, B. and Roether, W.: Meteor 06MT20011018 cruise data from the 2001 cruises, CARINA Data Set, available at: <http://cdiac.ornl.gov/ftp/oceans/CARINA/Meteor/06MT512/>, last access: 20 August 2015, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.CARINA\_06MT20011018, 2007.

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- Souvermezoglou, E., Krasakopoulou, E., and Goyet, C.: Total Inorganic Carbon and Total Alkalinity Distribution in the Aegean Sea, CIESM, Venice, Italy, 312 pp., 2010.
- Stone, M.: Cross validatory choice and assessment of statistical predictions, *J. Roy. Stat. Soc. B.*, 36, 111–147, 1974.
- 5 Taillandier, V., D'Ortenzio, F., and Antoine, D.: Carbon fluxes in the mixed layer of the Mediterranean Sea in the 1980s and the 2000s, *Deep-Sea Res. Pt. I*, 65, 73–84, 2012.
- Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., and Sutherland, S. C.: Seasonal variation of CO<sub>2</sub> and nutrients in the high-latitude surface oceans: a comparative study, *Global Biogeochem. Cy.*, 7, 843–878, 1993.
- 10 Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D. C. E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J., Arnarson, T. S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C. S., Delille, B., Bates, N. R., and de Baar, H. J. W.: Climatological mean and decadal change in surface ocean pCO<sub>2</sub>, and net sea-air CO<sub>2</sub> flux over the global oceans, *Deep-Sea Res. Pt. II*, 56, 554–577, 2009.
- Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G., Ho, C., Newberger, T., Sweeney, C., and Munro, D. R.: Climatological distributions of pH, pCO<sub>2</sub>, total CO<sub>2</sub>, alkalinity, and CaCO<sub>3</sub> saturation in the global surface ocean, and temporal changes at selected locations, *Mar. Chem.*, 164, 95–125, 2014.
- 20 Tanhua, T., Alvarez, M., and Mintrop, L.: Carbon dioxide, hydrographic, and chemical data obtained during the R/V Meteor MT84\_3 Mediterranean Sea cruise (5 April–28 April 2011), available at: [http://cdiac.ornl.gov/ftp/oceans/CLIVAR/Met\\_84\\_3\\_Med\\_Sea/](http://cdiac.ornl.gov/ftp/oceans/CLIVAR/Met_84_3_Med_Sea/), last access: 20 August 2015, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/OTG.CLIVAR\_06MT20110405, 2012.
- 25 Touratier, F. and Goyet, C.: Decadal evolution of anthropogenic CO<sub>2</sub> in the northwestern Mediterranean Sea from the mid-1990s to the mid-2000s, *Deep-Sea Res. Pt. I*, 56, 1708–1716, 2009.
- 30 Touratier, F. and Goyet, C.: Impact of the Eastern Mediterranean transient on the distribution of anthropogenic CO<sub>2</sub> and first estimate of acidification for the Mediterranean Sea, *Deep-Sea Res. Pt. I*, 58, 1–15, 2011.



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Touratier, F., Guglielmi, V., Goyet, C., Prieur, L., Pujo-Pay, M., Conan, P., and Falco, C.: Distributions of the carbonate system properties, anthropogenic CO<sub>2</sub>, and acidification during the 2008 BOUM cruise (Mediterranean Sea), *Biogeosciences Discuss.*, 9, 2709–2753, doi:10.5194/bgd-9-2709-2012, 2012.

5 Wanninkhof, R., Park, G. -H., Takahashi, T., Sweeney, C., Feely, R., Nojiri, Y., Gruber, N., Doney, S. C., McKinley, G. A., Lenton, A., Le Quéré, C., Heinze, C., Schwinger, J., Graven, H., and Khatiwala, S.: Global ocean carbon uptake: magnitude, variability and trends, *Biogeosciences*, 10, 1983–2000, doi:10.5194/bg-10-1983-2013, 2013.

10 Watson, A. and Orr, J.: Carbon dioxide fluxes in the Global Ocean, in: *Ocean Biogeochemistry, Global Change – The IGBP Series (closed)*, edited by: Fasham, M. R., Springer, Berlin, Heidelberg, 2003.

15 Zweng, M. M., Reagan, J. R., Antonov, J. I., Locarnini, R. A., Mishonov, A. V., Boyer, T. P., Garcia, H. E., Baranova, O. K., Johnson, D. R., Seidov, D., and Biddle, M. M.: *World Ocean Atlas 2013, Volume 2: Salinity*, edited by: Levitus, S. and Mishonov, A., Technical Edn., NOAA Atlas Nesdis 74, Silver Spring, MD, 39 pp., 2013.

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**Table 1.** List of available carbonate system datasets for the Mediterranean Sea.

Dataset	Period	Carbonate system parameters	Reference
Prosope	Sep–Oct 1999	$A_T$ and pH	Bégovic and Copin (2013)
Meteor 51/2	Oct–Nov 2001	$A_T$ and $C_T$	Schneider and Roether (2007)
Meteor 84/3	Apr 2004	$A_T$ , $C_T$ and pH	Tanhua et al. (2012)
Carbogib 2–6	2005–2006	$A_T$ and pH	Huertas (2007a–e)
Gift 1–3	2005–2006	$A_T$ and pH	Huertas (2007f–h)
Transmed	Jun 2007	$A_T$ and pH	Rivaro et al. (2010)
Sesame IT-4	Mar–Apr 2008	$A_T$ and $C_T$	SeaDataNet
Boum	Jun–Jul 2008	$A_T$ and $C_T$	Touratier et al. (2012)
Pacific–Celebes	2007–2009	$A_T$ and $C_T$	Hydes et al. (2012)
Moose-GE	May 2010	$A_T$ and $C_T$	SeaDataNet
Hesperides	May 2013	$A_T$	Perez et al. (2013)
MedSEA	May 2013	$A_T$ and $C_T$	Goyet et al. (2015)
Dyfamed time-series	1998–2013	$A_T$ and $C_T$	Oceanological Observatory of Villefranche-sur-Mer

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**Table 2.** Second order polynomial fit to derive  $A_T$  from salinity and temperature in the Mediterranean Sea surface waters.

Polynomial fit	$N$	$r^2$	RMSE ( $\mu\text{mol kg}^{-1}$ )
Eq. (1): $A_T = 2558.4 + 49.83(S - 38.2) - 3.89(T - 18) - 3.12(S - 38.2)^2 - 1.06(T - 18)^2$ $T > 13^\circ\text{C}$ and $36.30 < S < 39.65$	375	0.96	10.6

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**Table 3.** Performance of the different parameterizations for the estimation of  $A_T$  applied independently to the training dataset of this study.

Region	Parameterization	RMSE ( $\mu\text{mol kg}^{-1}$ )	$r^2$	Reference
Alboran Sea	$A_T = 94.85(S) - 1072.6$	$\pm 16.61$	0.92	Copin-Montégut (1993)
Dyfamed site	$A_T = 93.99(S) - 1038.1$	$\pm 16.31$	0.92	Copin-Montégut and Bégovic (2002)
Strait of Gibraltar	$A_T = 92.28(S) - 968.7$	$\pm 16.48$	0.92	Santana-Casiano et al. (2002)
Mediterranean Sea	$A_T = 73.7(S) - 285.7$	$\pm 26.11$	0.68	Schneider et al. (2007)
Dyfamed site	$A_T = 99.26(S) - 1238.4$	$\pm 18.53$	0.91	Touratier and Goyet (2009)
Western Mediterranean	$A_T = 95.25(S) - 1089.3$	$\pm 16.97$	0.92	Rivaro et al. (2010)
Eastern Mediterranean	$A_T = 80.04(S) - 499.8$	$\pm 14.58$	0.91	
Mediterranean Sea	$A_T = 1/(6.57 \times 10^{-5} + 1.77 \times 10^{-2})/S - (5.93 - 10^{-4}(\ln \theta)/\theta^2)$	$\pm 13.81$	0.92	Touratier and Goyet (2011)
Global relationship (Sub-tropics)	$A_T = 2305 + 58.66(S - 35) + 2.32(S - 35)^2 + 1.41(T - 20) + 0.04(T - 20)^2$	$\pm 40.50$	0.26	Lee et al. (2006)

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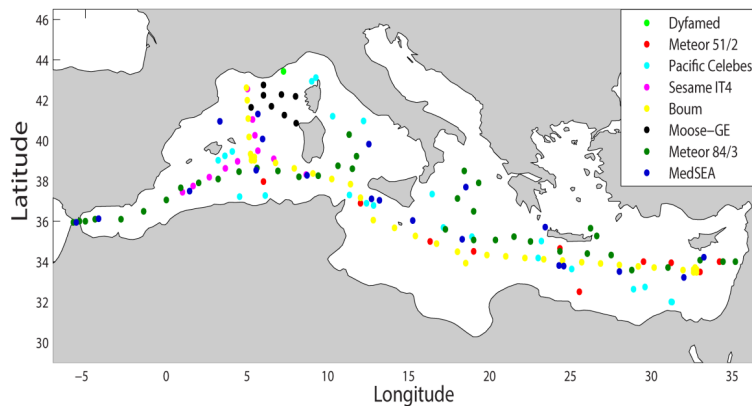


**Table 4.** Third order polynomial fit to derive  $C_T$  from salinity and temperature in the Mediterranean Sea surface waters.

Polynomial fit	N	$r^2$	RMSE ( $\mu\text{mol kg}^{-1}$ )
Eq. (2): $C_T = 2234 + 38.15(S - 38.2) - 14.38(T - 17.7) - 4.48(S - 38.2)^2 - 1.43(S - 38.2)(T - 17.7) + 9.62(T - 17.7)^2 - 1.10(S - 38.2)^3 + 3.53(T - 17.7)(S - 38.2)^2 + 1.47(S - 38.2)(T - 17.7)^2 - 4.61(T - 17.7)^3$ $T > 13^\circ\text{C}$ and $36.30 < S < 39.65$	381	0.90	14.3

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**Figure 1.** Spatial distribution of data points used to initiate the fits of  $A_T$  and  $C_T$ .

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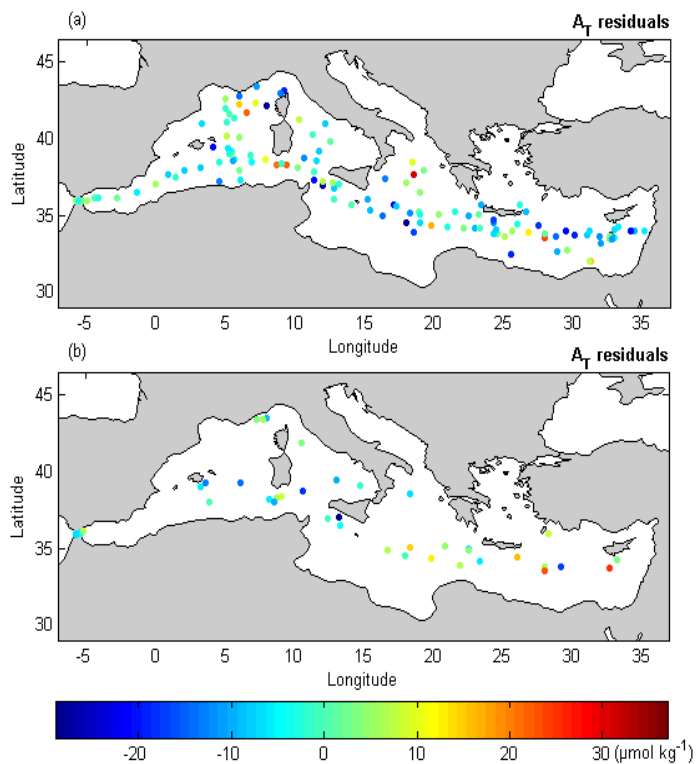
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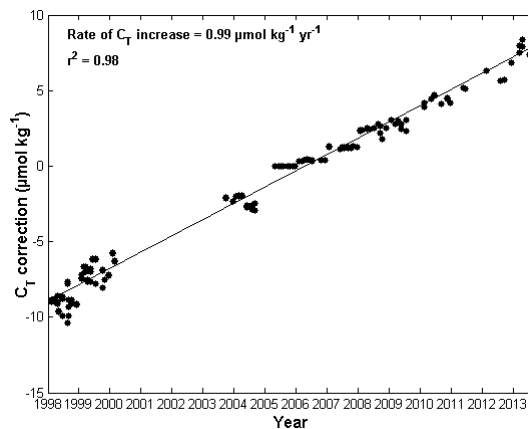
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**Figure 2.** Map of the residuals of the  $A_T$  algorithm (Table 1; Eq. 1) applied the (a) training and (b) testing datasets.

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**Figure 3.** Rate of increase applied to correct the  $C_T$  measurements in reference to the year 2005.

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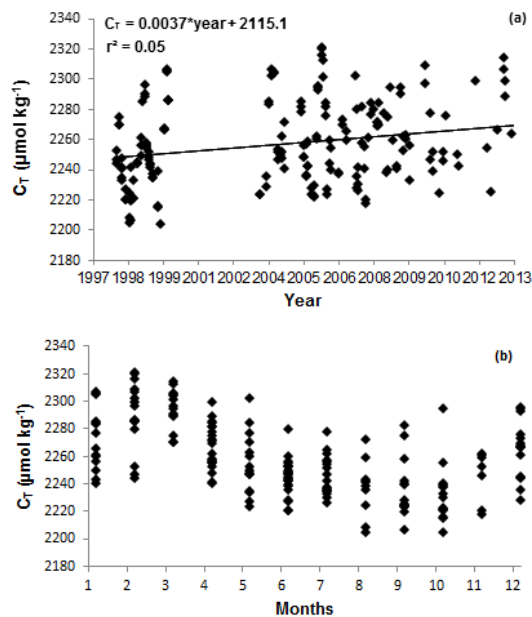
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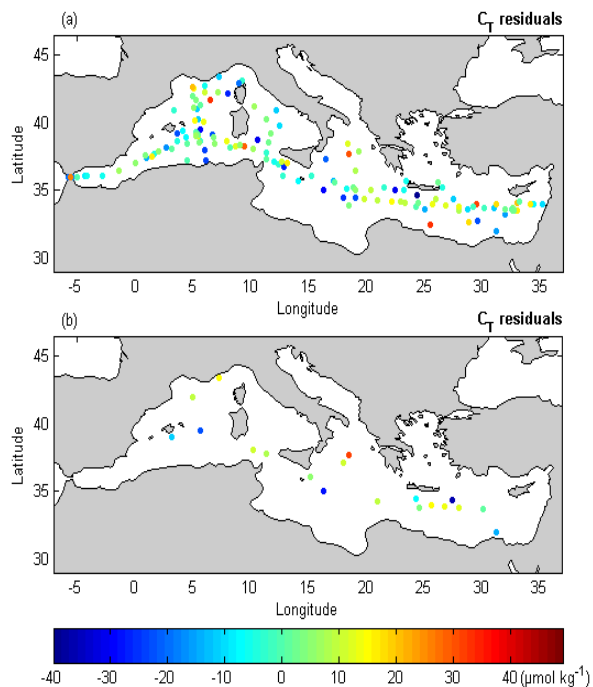
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**Figure 4.** (a) Temporal and (b) seasonal variations of  $C_T$  measured at the Dyfamed time-series station between 1998 and 2013.

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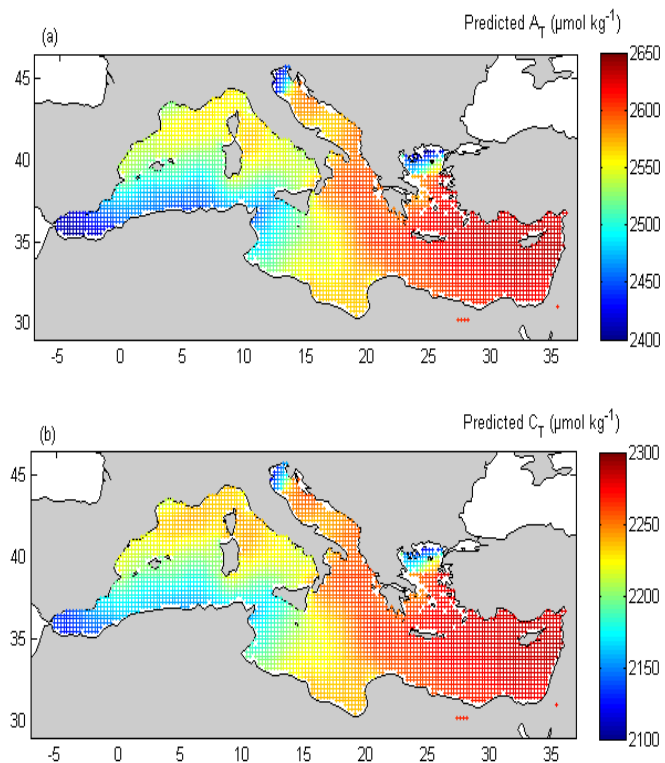


**Figure 5.** Comparison of the predicted  $C_T$  values from the  $C_T$  algorithm given in Table 1 – Eq. (2) with measurements which are (a) included or (b) excluded when deriving the fit.

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**Figure 6.** The seven years averages spatial variability of (a) surface  $A_T$  predicted from Eq. (1) and (b) surface  $C_T$  predicted from Eq. (2), applied to the 2005–2012 climatological fields of  $S$  and  $T$  from the WOA13.

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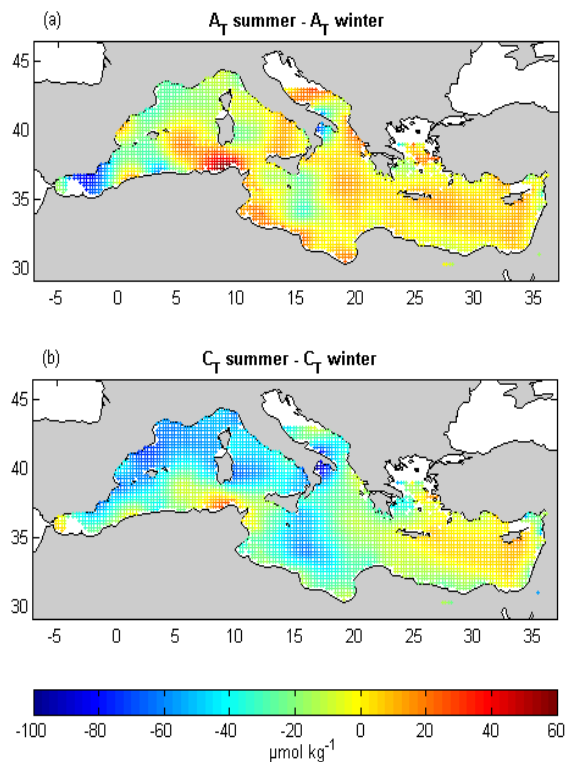
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**Figure 7.** Distribution of the summer-winter differences of (a) surface  $A_T$  predicted from Eq. (1) and (b) surface  $C_T$  predicted from Eq. (2), applied to the 2005–2012 climatological fields of  $S$  and  $T$  from the WOA13.